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Methyl C–H activation of 2,4,5-trimethylthiazole by a triosmium cluster: X-ray structures of $[(\mu\text{-H})Os_3(CO)_{10}\{\mu\text{-}\eta^2\text{-}CH_2C{=}NC(CH_3){=}C(CH_3)S\}]$ and $[(\mu\text{-H})_2Os_3(CO)_9\{\mu^3\text{-}\eta^2\text{-}CHC{=}C(CH_3)SC(CH_3)C{=}N\}]$

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Abstract

Treatment of $[Os_3(CO)_{10}(MeCN)_2]$ with 2,4,5-trimethylthiazole at 25 °C leads to two new isomeric compounds $[(\mu\text{-H})Os_3(CO)_{10}\{\mu\text{-}\eta^2\text{-}CH_2C{=}NC(CH_3){=}C(CH_3)S\}]$ (**1**) and $[(\mu\text{-H})Os_3(CO)_{10}\{\mu\text{-}\eta^2\text{-}CH_2\text{–}C{=}C(CH_3)SC(CH_3){=}N\}]$ (**2**) and the previously reported compounds $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-Cl})]$ (**4**) and $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OH})]$ (**5**). Compounds **1** and **2**, formed from activation of C-2 and C-4 methyl substituents of the ligand, respectively, undergo decarbonylation and further C–H activation of the coordinated methylidene group at 110 °C to give $[(\mu\text{-H})_2Os_3(CO)_9\{\mu^3\text{-}\eta^2\text{-}CHC{=}NC(CH_3){=}C(CH_3)S\}]$ (**6**) and $[(\mu\text{-H})_2Os_3(CO)_9\{\mu^3\text{-}\eta^2\text{-}CHC{=}C(CH_3)SC(CH_3){=}N\}]$ (**7**). The compounds have been characterized by spectroscopic data together with single crystal X-ray diffraction studies for **1** and **7**.

Keywords: Osmium; Metallation; Methyl substituent; Trimethylthiazole; X-ray structures

1. Introduction

Currently, there is considerable interest in the reactivity of N- and S-containing small heterocyclic organic molecules towards transition metal carbonyl clusters because such ligands frequently stabilize the metal cluster framework by serving as chelating or bridging ligands [1–5]. We have previously investigated the reactions of benzothiazole [6], benzimidazole-2-thione [6], thiomorpholine [7], thiazolidine [7], 4-methylthiazole [8], thiazole [9,10], pyridine-2-thione [11] and pyrimidine-2-thione [11] with osmium and ruthenium carbonyl clusters and observed a remarkable influence on the type of product obtained depending on the metal carbonyl clusters, the heterocycles and the reaction conditions. For example, thiomorpholine (C_4H_9NS) reacts with $[Ru_3(CO)_{12}]$ at 68 °C to give $[(\mu\text{-H})Ru_3(CO)_9(\mu\text{-}\eta^2\text{-}SCH_2CH_2NH_2)]$ by a ring opening reaction of the ligand followed by elimination of C2 fragment whereas thiazolidine (C_3H_7NS) under identical conditions gives the dicnuclear compound $[Ru_2(CO)_6(\mu\text{-}\eta^3\text{-}SCH_2CH_2NHCH_2)]$ formed also by ring-opening cleavage of the C–S bond of thiazolidine [7]. Furthermore, thiazole reacts with $[Ru_3(CO)_{12}]$ in presence of sodium benzophenone ketyl at 65 °C to give the pentaruthenium cluster $[(\mu\text{-H})Ru_3(CO)_9(\mu^5\text{-}\eta^5\text{-}HC{=}NC{=}CHS)(\mu\text{-H})Ru_2(CO)_4(\eta^1\text{-}HC{=}NCH{=}CHS)(\mu\text{-}2,3\text{-}\eta^3\text{-}C{=}NCH{=}CHS)]$ containing three thiazole derived ligands in different coordination modes whereas with $[Os_3(CO)_{10}(MeCN)_2]$ at 25 °C, it forms two isomeric compounds $[(\mu\text{-H})Os_3(CO)_{10}\{\mu\text{-}2,3\text{-}\eta^2\text{-}C{=}NCH{=}CHS\}]$ and $[(\mu\text{-H})Os_3(CO)_{10}\{\mu\text{-}3,4\text{-}\eta^2\text{-}HC{=}NC{=}HCHS\}]$ by matallation at 2- and 4-positions, respectively [9,10].

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In contrast to the numerous examples of the ortho-metallation chemistry of five- and six-membered aromatic and aliphatic cyclic compounds, activation of the sp^3 C–H bond is rare, since sp^3 C–H bond activation is difficult because the sp^3 C–H σ^* orbital is at a higher energy and its s orbital is at a low energy [12]. Many experimental efforts have been made to perform sp^3 C–H activation by using highly reactive transition metal complexes [13–18]. Lewis and co-workers [19] reported the ethenyl group C–H activation of 2-ethenyl pyridine leading to the formation of $[(\mu\text{-H})(Os_3(CO)_{10}(NC_5H_4C{=}CH)]$. We have recently reported [20] the methyl activation of 2-methyl-2-thiazoline when it reacted with $[Os_3(CO)_{10}(MeCN)_2]$ affording $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}CH_2C{=}NCH_2CH_2S)]$ (**3**). As part of our on going studies on the reactivity of N- and S-containing heterocycles, we herein report on the reaction of 2,4,5-trimethylthiazole with $[Os_3(CO)_{10}(MeCN)_2]$. The reaction products have been charactersied by spectroscopic data, and two of these $[(\mu\text{-H})Os_3(CO)_{10}\{\mu\text{-}\eta^2\text{-}CH_2C{=}NC(CH_3){=}C(CH_3)S\}]$ (**1**) and $[(\mu\text{-H})_2Os_3(CO)_9\{\mu^3\text{-}\eta^2\text{-}CHC{=}C(CH_3)SC(CH_3)C{=}N\}]$ (**7**) have also been structurally characterized by X-ray crystallography.

2. Results and discussion

The lightly stabilized cluster $[Os_3(CO)_{10}(MeCN)_2]$ reacts with 2,4,5-trimethylthiazole at room temperature to give two isomeric compounds $[(\mu\text{-H})Os_3(CO)_{10}\{\mu\text{-}\eta^2\text{-}CH_2C{=}N{-}C(CH_3){=}C(CH_3)S\}]$ (**1**) and $[(\mu\text{-H})Os_3(CO)_{10}\{\mu\text{-}\eta^2\text{-}CH_2{-}C{=}C(CH_3)SC(CH_3){=}N\}]$ (**2**) in **9** and 20% yields, respectively together with the known compounds $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-Cl})]$ (**4**) and $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OH})]$ (**5**). Both compounds **1** and **2** have been characterized by elemental analysis, infrared, ^{1}H NMR and mass spectroscopic data together with a single crystal X-ray analysis for **1**. The identity of **4** and **5** was confirmed by comparing their spectroscopic data with those reported for the independently prepared complexes [21,22]. The mass spectrum of **1** shows the molecular ion peak at m/z 977 corresponding to the formulation of **1**. The carbonyl stretching frequencies of **1** in both the appearance and position of the bands are very similar to those of **3** [20] indicating that they have very similar distribution of the carbonyl ligands. The ^{1}H NMR spectrum of **1** in the aliphatic region shows two doublets at δ 2.70 and 2.15 ($J = 20.0$ Hz) for the methylidene protons and two singlets at δ 2.30 and 2.24 for the methyl protons in a relative intensity of 1:1:3:3, respectively. The chemical shifts and magnitude of coupling constant of the methylidene protons are comparable to those reported for **3** (δ 1.81 and 2.40, $J = 20.0$ Hz) [20]. The hydride region of the spectrum contains a singlet at δ −13.45. Thus the ^{1}H NMR data is indicative of the C–H bond activation of a methyl substituent of 2,4,5-trimethylthiazole ligand and subsequent coordination of the carbon to the metal.

The disposition of the ligands in **1** was determined by X-ray crystallography. The structure of **1** is shown in Fig. 1 and selected bond distances and angles are given in Table 1. The compound consists of a triangular cluster of three osmium atoms with two relatively longer but almost equal [Os(1)–Os(2) = 2.9268(6), Os(2)–Os(3) = 2.9174(5) Å] and one shorter [Os(1)–Os(3) = 2.8795(6) Å] metal–metal bonds. The average Os–Os distance of 2.908 Å is somewhat longer than the average value of 2.877(3) Å in $[Os_3(CO)_{12}]$ [23]. The metal atoms Os(3) and Os(2) each contains three terminal carbonyl ligands while Os(1) is bonded to four. The hydride ligand bridges the Os(2)–Os(3) edge. An interesting feature of this structure is the activation of 2-methyl substituent of the thiazole ligand during the reaction leading to the formation of 4,5-dimethyl-2-methylidenethiazole ligand. This methylidene ligand is η^2-coordinated to the hydride bridged Os(2)–Os(3) edge through a one electron metal–carbon σ bond from C(11) to Os(2) and a two electron dative bond from N(1) to Os(3). The Os(2)–C(11) bond length of 2.216(10) and the Os(3)–N(1) bond length of 2.000(9) Å are comparable to those reported for the related compound **3** [20]. The N(1)–C(12) bond is short, 1.337 (11) Å, and consistent with its double bond character while the N(1)–C(14) bond is longer at 1.394(14) Å. The C–S bond distances of 1.688(11) and 1.749(10) Å are shorter compared to the C–S distances of 1.747(11) and 1.778(11) Å observed in **3** [20]. The organic ligand is nearly perpendicular to the plane of the osmium triangle as shown by the N(1)–Os(3)–Os(1) and C(11)–Os(2)–Os(1) angles of 92.0(2)° and 90.1°, respectively. Overall,

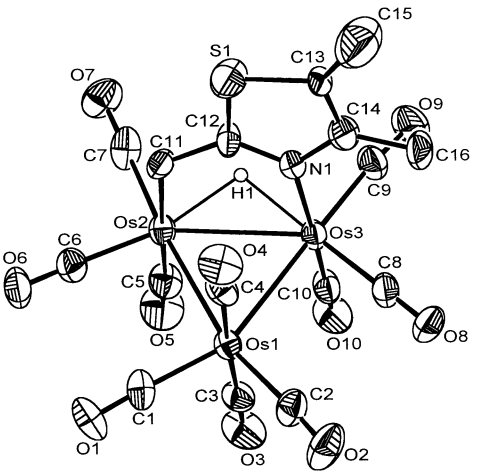


Fig. 1. X-ray structure of $[(\mu\text{-H})Os_3(CO)_{10}\{\mu\text{-}\eta^2\text{-}CH_2C{=}NC(CH_3){=}C(CH_3)S\}]$ (**1**) with atom labeling scheme. Thermal ellipsoids are drawn at 35% probability level. The hydrogen atoms except the bridging hydride are omitted for clarity.

Table 1
Bond lengths (Å) and angles (°) for **1**

Bond lengths			
Os(1)–Os(2)	2.9268(6)	Os(1)–Os(3)	2.8795(6)
Os(2)–Os(3)	2.9174(5)	Os(2)–C(11)	2.216(10)
Os(3)–N(1)	2.200(9)	S(1)–C(12)	1.688(11)
S(1)–C(13)	1.749(10)	N(1)–C(12)	1.337(11)
N(1)–C(14)	1.394(14)	C(11)–C(12)	1.478(14)
Os(2)–H(1)	1.85 ^{a}	Os(3)–H(1)	1.91 ^{a}
Os–C(CO)	1.91(2) ^{b}	C–O	1.14(2) ^{b}
Bond angles			
C(1)–Os(1)–C(2)	100.8(5)	C(1)–Os(1)–C(4)	92.1(4)
C(2)–Os(1)–C(4)	89.5(5)	C(1)–Os(1)–C(3)	91.3(5)
C(2)–Os(1)–C(3)	90.7(5)	C(4)–Os(1)–C(3)	176.5(5)
C(7)–Os(2)–C(6)	93.8(5)	C(7)–Os(2)–C(5)	92.9(5)
C(6)–Os(2)–C(5)	93.2(5)	C(7)–Os(2)–C(11)	83.5(5)
C(6)–Os(2)–C(11)	89.5(4)	C(5)–Os(2)–C(11)	175.7(5)
C(8)–Os(3)–C(10)	89.0(5)	C(8)–Os(3)–C(9)	98.2(5)
C(10)–Os(3)–C(9)	87.6(5)	C(8)–Os(3)–N(1)	98.0(4)
C(10)–Os(3)–N(1)	172.6(4)	C(9)–Os(3)–N(1)	89.0(4)
C(12)–S(1)–C(13)	94.0(5)	C(12)–N(1)–C(14)	111.8(9)
C(12)–N(1)–Os(3)	122.4(7)	C(14)–N(1)–Os(3)	125.1(7)
C(12)–C(11)–Os(2)	117.8(6)	N(1)–C(12)–C(11)	127.9(9)
N(1)–C(12)–S(1)	112.8(8)	C(11)–C(12)–S(1)	118.9(7)
Os–C–O	175.8(2) ^{b}		

[a] Approximate values.
[b] Average values.

the cluster is structurally very similar to related triosmium cluster **3** [20].

The ν(CO) stretching frequencies of **2** are very similar to those of **1** indicating that compounds **1** and **2** are a structurally analogous pair of isomers. The mass spectrum shows the molecular ion peak at m/z 977 and other important peaks due to the sequential loss of ten carbonyl groups. The ^{1}H NMR spectrum of **2** displays a singlet hydride resonance at δ −13.64, two doublets at δ 3.01 and 2.31 ($J = 19.6$ Hz) for the methylidene protons and two singlets at δ 2.48 and 2.24 arising from the methyl protons of the ligand. Assuming compound **2** has the same basic features as **1**, it is concluded that **2** results from C–H activation of 4-methyl group of the ligand.

Thermolysis of both **1** and **2** in refluxing toluene at 110 °C yields the methylidyne compounds $[(\mu\text{-H})_2Os_3(CO)_9\{\mu\text{-}\eta^2\text{-CHC=NC(CH}_3\text{)=C(CH}_3\text{)S}\}]$ (**6**) and $[(\mu\text{-H})_2Os_3(CO)_9\{\mu_3\text{-}\eta^2\text{-CHC=C(CH}_3\text{)SC(CH}_3\text{)=N}\}]$ (**7**), respectively by a further C–H oxidation addition of the coordinated methylidene group.

The structure of **7**, shown in Fig. 2, was also determined by X-ray crystallography. Selected bond distances and angles for this compound are given in Table 2. The molecule consists of Os_3 triangle with one significantly longer [Os(1)–Os(3) = 3.0131(6) Å] and two shorter Os–Os edges [Os(1)–Os(2) = 2.8173(6), [Os(2)–Os(3) = 2.8165(6). Each osmium contains three terminal carbonyl groups. The Os(1)–Os(2) edge is simultaneously bridged by a hydride and methylidyne carbon atom. The 2,5-dimethyl-4-methylidynethiazole ligand donates four electrons via a two electron lone pair bond from N(1) to Os(3) and two one electron σ-bonds from C(10) to Os(2) and Os(1). The Os(3)–N(1) bond length of 2.138(9) Å is comparable to the corresponding bond length in $[(\mu\text{-H})_2Os_3(CO)_9\{\mu\text{-}\eta^2\text{-CHC=NCH}_2CH_2CH_2]$ [24]. The methylidyne bridge is almost symmetrical {Os(1)–C(10) = 2.156(11) and

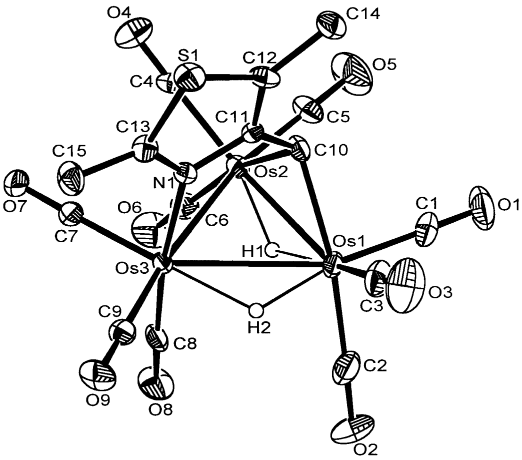


Fig. 2. X-ray structure of $[(\mu\text{-H})_2Os_3(CO)_9\{\mu_3\text{-}\eta^2\text{-CHC=C(CH}_3\text{)SC(CH}_3\text{)=N}\}]$ (**7**) with atom labeling scheme. Thermal ellipsoids are drawn at 35% probability level. The hydrogen atoms except the bridging hydrides are omitted for clarity.

Table 2
Bond lengths (Å) and angles (°) for **7**

Bond lengths			
Os(1)–Os(2)	2.8173(6)	Os(2)–Os(3)	2.8165(6)
Os(1)–Os(3)	3.0131(6)	Os(1)–C(10)	2.156(11)
Os(2)–C(10)	2.160(11)	Os(3)–N(1)	2.138(9)
S(1)–C(13)	1.709(12)	S(1)–C(12)	1.719(12)
N(1)–C(13)	1.327(14)	N(1)–C(11)	1.393(13)
C(10)–C(11)	1.453(15)	Os(1)–H(1)	1.99 ^{a}
Os(2)–H(1)	1.59 ^{a}	Os(1)–H(2)	1.61 ^{a}
Os(3)–H(2)	1.84 ^{a}	Os–C(CO)	1.91(2) ^{b}
C–O	1.14(2) ^{b}		
Bond angles			
C(1)–Os(1)–C(3)	91.5(6)	C(1)–Os(1)–C(2)	94.4(6)
C(3)–Os(1)–C(2)	96.8(7)	C(1)–Os(1)–C(10)	89.8(5)
C(3)–Os(1)–C(10)	94.8(5)	C(2)–Os(1)–C(10)	167.5(5)
C(5)–Os(2)–C(4)	94.7(5)	C(5)–Os(2)–C(6)	95.2(5)
C(4)–Os(2)–C(6)	97.0(5)	C(5)–Os(2)–C(10)	92.6(5)
C(4)–Os(2)–C(10)	92.3(5)	C(6)–Os(2)–C(10)	167.3(5)
C(8)–Os(3)–C(7)	92.7(5)	C(8)–Os(3)–C(9)	93.0(5)
C(7)–Os(3)–C(9)	100.7(5)	C(8)–Os(3)–N(1)	170.9(4)
C(7)–Os(3)–N(1)	91.3(4)	C(9)–Os(3)–N(1)	94.3(4)
C(13)–S(1)–C(12)	91.8(5)	C(13)–N(1)–C(11)	113.3(9)
C(13)–N(1)–Os(3)	130.2(8)	C(11)–N(1)–Os(3)	116.5(7)
C(11)–C(10)–Os(1)	118.2(8)	C(11)–C(10)–Os(2)	115.8(7)
Os(1)–C(10)–Os(2)	81.5(4)	C(12)–C(11)–N(1)	112.9(9)
C(12)–C(11)–C(10)	127.6(10)	N(1)–C(11)–C(10)	119.4(9)
Os–C–O	177.7(9) ^{b}		

[a] Approximate values.
[b] Average values.

Os(2)–C(10) = 2.160(11) Å}. The short N(1)–C(13) bond distance of 1.327 (14) Å is indicative of a double bond, while the N(1)–C(11) bond length of 1.393(14) Å is closer to a single bond. The S–C distances 1.719(12) and 1.709 Å are shorter than that expected for a S–C single bond (1.79 Å) [25].

The spectroscopic data of **7** are consistent with the solid-state structure. The hydride region of the ^{1}H NMR spectrum contains two hydride resonances, a singlet at δ -15.41 and a doublet at δ -14.74 ($J = 1.6$ Hz). The aliphatic region contains a doublet at δ 5.22, due to the methine proton and two singlets at δ 2.18 and 2.50 due to the methyl protons.

The structural assignment for **6** is based on spectroscopic data. The carbonyl stretching frequences of **6** are very similar to those of **7**, hence the compounds are assumed to be structurally similar. The ^{1}H NMR spectrum contains a doublet at δ 5.20 ($J = 1.6$ Hz) for the methylidene proton, two slinglets at δ 2.46 and 2.15 for the methyl protons in a relative intensity of 1:3:3. The hydride region of the spectrum contains two resonances, one is a doublet at δ -14.70 ($J = 1.6$ Hz) due to coupling to the methylidyne proton and the other is a singlet at δ -15.44. The hydrides chemical shifts of **6** are very similar to those observed for **7**, suggesting again their structural similarity.

In summary, the most significant aspect of this work is the ambient temperature carbon–hydrogen activation of the methyl substituents of 2,4,5-trimethylthiazole leading to the isolation of two isomeric methylidene compounds **1** and **2**. Thermolysis of **1** and **2** at 110 °C gives the isomeric methylidyne complexes **6** and **7** by decarbonylation and further C–H activation. The solid-state structures of **1** and **7** demonstrate that **1** and **6** are formed by C(2)–methyl bond activation while **2** and **7** are formed by C(4)–methyl bond activation of 2,4,5-trimethylthiazole. Attempts to further activate the C–H bond of **6** and **7** in refluxing octane have thus far been unsuccessful.

3. Experimental

3.1. General

All reactions were performed under a nitrogen atmosphere. Reagent grade solvents were freshly distilled from the appropriate drying agents. IR spectra were recorded on a Shimadzu FT IR 8101 spectrometer. ^{1}H NMR spectra were recorded on a Bruker DPX 400 spectrometer. 2,4,5-Trimethylthiazole was purchased from Merck and used as received. The compound $[Os_3(CO)_{10}(MeCN)_2]$ was prepared according to the published procedure [24].

3.2. Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with 2,4,5-trimethylthiazole

To a CH_2Cl_2 solution (25 cm^3) of $[Os_3(CO)_{10}(MeCN)_2]$ (0.220 g, 0.236 mmol) was added 2,4,5-trimethylthiazole (0.165 g, 1.296 mmol) and the mixture was stirred at room temperature (r.t.) for 72 h. The volatiles were removed under reduced pressure and the residue was chromatographed by TLC on silica gel. Elution with C_6H_{14}/CH_2Cl_2 (9:1, v/v) developed one major and two minor bands. The minor bands afforded $[(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}Cl)]$ (**4**) (0.006 g, 3%) and $[(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}OH)]$ (**5**) (0.012 g, 6%). Rechromatography of the major band followed by repeated fractional crystallization afforded pure $[(\mu\text{-}H)Os_3(CO)_{10}\{\mu\text{-}\eta^2\text{-}CH_2C{=}NC(CH_3){=}C(CH_3)S\}]$ (**1**) (0.021 g, 9%) and $[(\mu\text{-}H)Os_3(CO)_{10}\{\mu\text{-}\eta^2\text{-}CH_2\text{–}C{=}C(CH_3)SC(CH_3){=}N\}]$ (**2**) (0.046 g, 20%) as yellow crystals.

3.2.1. Analytical and spectroscopic data for **1** and **2**

Anal. Calc. for $C_{16}H_9NO_{10}Os_3S$ (**1**): C, 19.65; H, 0.93; N, 1.43. Found: C, 19.76; H, 0.98; N, 1.48%. IR (C_6H_{14}): νCO 2102 m, 2059 vs, 2049 vs, 2020 s, 2003 s, 1998 s, 1988 s, 1978 w, 1973 w cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.70 (d, 1H, $J = 20.0$ Hz); 2.24 (d, 1H, $J = 20.0$ Hz); 2.30 (s, 3H); 2.15 (s, 3H); -13.45 (s, 1H); Mass spectrum: m/z 977 ($[M^+]$). *Anal*. Calc. for $C_{16}H_9NO_{10}Os_3S$ (**2**): C, 19.65; H, 0.93; N, 1.43. Found: C, 19.68; H, 0.95; N, 1.40%. IR (C_6H_{14}): νCO 2101 m, 2057 vs, 2047 vs, 2020 s, 2002 s, 1965 s, 1988 s, 1976 w, 1972 w cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.01 (d, 1H, $J = 19.6$ Hz); 2.48 (s, 3H); 2.31 (s, 1H, $J = 19.6$ Hz); 2.24 (s, 3H); -13.64 (s, 1H); Mass spectrum: m/z 977 ($[M^+]$).

3.3. Thermolysis of **1**

A $C_6H_5CH_3$ solution of **1** (0.025 g, 0.026 mmol) was heated to reflux for 13 h. The solvent was removed under reduced pressure and the residue was chromatographed by TLC on silica gel. Elution with C_6H_{14} gave two bands. The faster moving band gave $[(\mu\text{-}H)_2Os_3(CO)_9\{\mu_3\text{-}\eta^2\text{-}CHC{=}NC(CH_3){=}C(CH_3)S\}]$ (**6**) (0.016 g, 67%) as yellow crystals from C_6H_{14}/CH_2Cl_2 at -20 °C. *Anal*. Calc. for $C_{15}H_9NO_9Os_3S$: C, 18.96; H, 0.96; N, 1.47. Found: C, 19.25; H, 0.99; N, 1.58%. IR (C_6H_{14}): νCO 2097 m, 2072 vs, 2045 s, 2029 m, 2000 m, 1989 m, 1970 m cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.20 (d, 1H, $J = 1.6$ Hz); 2.46 (s, 3H); 2.15 (s, 3H); -14.70 (d, 1H, $J = 1.6$ Hz); -15.44 (d, 1H, $J = 1.6$ Hz); Mass spectrum: m/z 949 ($[M^+]$). The slower moving band afforded unreacted **1** (0.005 g).

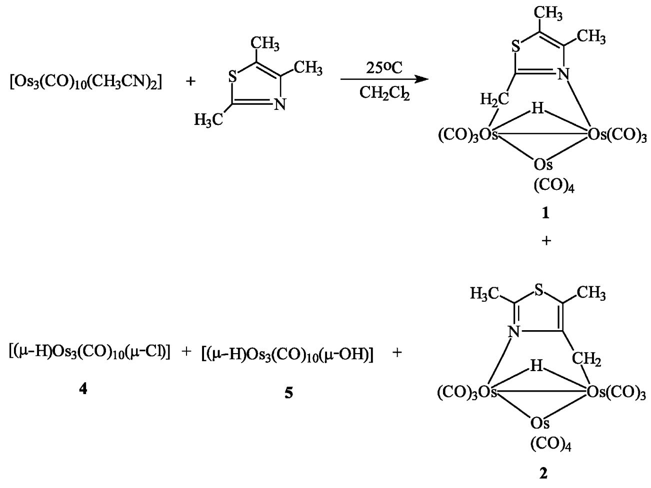
3.4. Thermolysis of **2**

A similar thermolysis to that above of **2** (0.050 g, 0.052 mmol) followed by similar work up afforded [(μ-

Table 3
Crystal data and structure refinement for **1** and **7**

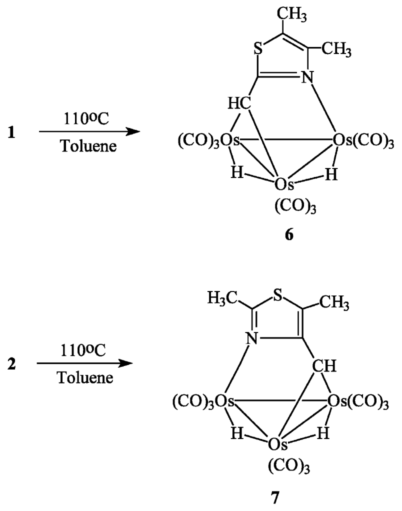
Compound	**1**	**7**
Empirical formula	$C_{16}H_9NO_{10}Os_3S$	$C_{15}H_9NO_9Os_3S$
Formula weight	977.90	949.89
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	8.9141(4)	8.2406(5)
b (Å)	14.3937(4)	9.7031(5)
c (Å)	17.1568(8)	14.5421(12)
α (°)	–	88.010(5)
β (°)	93.374(2)	74.519(7)
γ (°)	–	74.079(5)
Volume (Å^3)	2197.5(2)	1076.68(12)
Z	4	2
D_{calc} (g cm^{-3})	2.956	2.930
Absorption coefficient (cm^{-1})	17.450	17.800
Crystal size (mm)	0.15 × 0.12 × 0.12	0.25 × 0.20 × 0.20
θ Range for data collection (°)	1.85–26.04	1.45–25.10
Reflections collected	15 014	4119
Independent reflections	4297 [$R_{int} = 0.0580$]	3826 [$R_{int} = 0.0166$]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0454$, $wR_2 = 0.0987$	$R_1 = 0.0389$, $wR_2 = 0.1154$
R indices (all data)	$R_1 = 0.0682$, $wR_2 = 0.1089$	$R_1 = 0.0475$, $wR_2 = 0.1204$
Goodness-of-fit on F^2	1.001	1.073

Details in common: λ(Mo Kα) = 0.71073 Å, T = 150 K, yellow prisms, full-matrix least-squares refinement on F^2 using all unique data.



Scheme 1.

H)$_2$Os$_3$(CO)$_9${μ$_3$-η^2-CHC=C(CH$_3$)SC(CH$_3$)=N}] (**7**) (0.036 g, 73%) as yellow crystals from C_6H_{14}/CH_2Cl_2 at −15 °C. *Anal*. Calc. for $C_{15}H_9NO_9Os_3S$: C, 18.96; H, 0.96; N, 1.47. Found: C, 19.32; H, 1.12; N, 1.52%. IR (C_6H_{14}): νCO 2098 m, 2074 s, 2046 s, 2012 s, 2002 m, 1989 m, 1971 m cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 5.22 (d, 1H, J = 1.6 Hz), 2.50 (s, 3H), 2.18 (s, 3H), −15.41 (s, 1H), −14.70 (d, 1H, J = 1.6 Hz); Mass spectrum: m/z 949 ([M^+]).



Scheme 2.

3.5. Single crystal X-ray structure determination of 1 and 7

Suitable crystals of **1** and **7** for X-ray diffraction studies were obtained by crystallization from C_6H_{14}/CH_2Cl_2 mixture by slow evaporation of the solvents at r.t. Crystallographic data for **1** were collected at 150 K, using a Bruker–Nonius CCD area detector diffractometer and Mo Kα radiation (λ = 0.71073 Å). The crystal-to-detector distance was 32 mm, and ϕ and ω scans (1.2° increments, 15 s exposure time) were carried out to fill the Ewald sphere. Data collection and processing were carried out using the programs COLLECT [26] and DENZO [27]. Empirical absorption corrections were applied to the data set using multiple and symmetry-related data measurements via the program SORTAV [28]. The unit cell was indexed from all observed reflections in a ϕ range of 10° and refined using the entire data set. The unit cell parameters and intensity data for **7** were collected at 150 K using a CAD4 diffractometer (ω scan) and Mo Kα radiation (λ = 0.71073 Å). Empirical absorption corrections were also applied to this data set using the ψ-scan method [29]. The structures were solved by direct methods (SHELXS-96) [30] and refined on F^2 by full-matrix least-squares (SHELXL-97) [31] using all unique data. The non-hydrogen atoms were refined with anisotropic displacement coefficients. The bridging hydrides in both structures were located from difference maps but not refined. Other hydrogen atoms were included in calculated positions (riding model). The crystal data and details of refinements are summarized in Table 3 (Schemes 1 and 2).

4. Supplementary data

The full crystallographic data for these compounds have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 192332 and 192333 for compounds **1** and **7**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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